

⑫

EUROPEAN PATENT SPECIFICATION

⑬ Date of publication of patent specification: 25.04.90

⑭ Int. Cl.⁵: **A 61 K 7/16, A 61 K 7/18**

⑮ Application number: 83303588.4

⑯ Date of filing: 22.06.83

⑰ Improved dentifrice preparations comprising calcined kaolin abrasives.

⑱ Priority: 28.06.82 US 393046

⑲ Date of publication of application:
14.03.84 Bulletin 84/11

⑳ Publication of the grant of the patent:
25.04.90 Bulletin 90/17

㉑ Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

㉒ References cited:
WO-A-81/02670
US-A-3 105 013
US-A-3 282 792
US-A-4 108 979
US-A-4 108 981
US-A-4 122 163

H.JANISTYN "Handbuch der Kosmetika und
Riechstoffe", edition 3, vol. 1, 1978, Hüthig,
Heidelberg, page 936

㉓ Proprietor: INDIANA UNIVERSITY
FOUNDATION
Showalter House P.O. Box 500
Bloomington Indiana 47402 (US)

㉔ Inventor: Muhler, Joseph Charles
Box 36
Howe Indiana 46746 (US)
Inventor: Putt, Mark S.
4034 Westlane Road
Fort Wayne Indiana 46815 (US)

㉕ Representative: Bull, Michael Alan et al
Haseftine Lake & Co. Hazlitt House 28
Southampton Buildings Chancery Lane
London WC2A 1AT (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

EP 0 102 695 B1

Description

Field of the invention

The present invention relates to new dentifrice cleaning and polishing agents and to the formulation and utilization of dentifrice preparations incorporating such cleaning and polishing agents. In particular, the invention relates to a dentifrice cleaning and polishing composition comprising calcined kaolin in combination with talc and preferably titanium dioxide.

Incorporation of talc into a calcined kaolin based dentifrice permits the rheological properties of the dentifrice to be significantly improved. The provision of a talc modifier also enhances the polishing ability of calcined kaolins, improves fluoride and stannous ion availability and reduces abrasion. Moreover, the addition of titanium dioxide permits these advantages to be achieved without sacrificing the desired whiteness of the dentifrice.

The compositions of this invention serve to clean and polish dental hard tissue in a novel manner such that reaccumulations of pellicle and materia alba and occurrence and reformation of plaque and calculus on oral hard tissue are markedly reduced, thereby significantly reducing the occurrence of gingivitis and other soft tissue and periodontal disease. Fluoride-containing anticariogenic adjuvants such as sodium fluoride, stannous fluoride, and, especially, 1:2 molar mixtures thereof, may also usefully be incorporated in such compositions.

Description of the prior art

Dental research has developed substantial evidence that beyond the age of thirty-five years loss of teeth is predominantly the result of periodontal involvement rather than dental caries. However, evidence in the literature suggests that gingivitis itself may be present in a large portion of the population at a much earlier age. In this form the disease is reversible. A major factor contributing to periodontal disease is the accumulation of certain forms of dental plaque and calculus (e.g., salivary tartar) on the teeth. These accumulations result in tissue inflammation of the surrounding gingiva, and, as the condition increases in severity, the periodontal fibers and supporting bone subsequently become affected. These reactions lead to the destruction of the supporting structures and the subsequent mass loss, in most instances, of sound teeth.

Heretofore, commercially available dentifrices containing abrasives such as insoluble sodium metaphosphate (NaPO_3), calcium hydrogen phosphate dihydrate/anhydrous calcium hydrogen phosphate, ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}/\text{CaHPO}_4$), calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$), and silica (SiO_2) have exhibited relatively unsatisfactory enamel-polishing qualities and consequently have not been wholly effective in preventing the reaccumulation of materia alba, oral debris, plaque, pellicle, exogenous stains, and dental calculus. In particular, while conventional cleaning and polishing agents used with a toothbrush are capable, to varying degrees, of removing materia alba, food particles, exogenous stains, and other tooth surface pigmentations when utilized in ordinary daily brushings, they have not exhibited the ability to remove the more resistant forms of enamel pigments and to produce a smooth tooth surface resistant to dental plaque and calculus formation. Furthermore, these conventional abrasives leave the teeth esthetically less desirable than would more effective polishing agents.

The beneficial effects, in terms of a reduction in the incidence of dental caries, resulting from the incorporation of water-soluble fluoride salts are well known. However, efforts to utilize such salts in dentifrices suitable for home use have been handicapped by the tendency for fluoride ions to be deactivated and rendered unavailable by other ingredients, particularly the abrasive component of such dentifrices. While generally speaking, dentifrice abrasives in therapeutic products used today are to varying degrees compatible with fluoride agents, there is a wide variation in compatibility. Calcium-containing abrasives are not particularly compatible. While the non-calcium-containing abrasives are somewhat more compatible, they frequently are inferior with regard to enamel polishing.

Saul et al., U.S. Patent No. 3,105,013 recommends using calcined aluminum silicate as a dental abrasive on the basis of its compatibility with fluoride adjuvants. However, the preferred material of Saul et al. is commercially available under the trademark "Kaopolite SF". Kaopolite SF is off-white in color and is thus esthetically undesirable in a commercial dentifrice.

Japanese Patent No. 24224/74 describes dental abrasives combining calcined kaolins with other abrasives such as calcium carbonate, calcium hydrogen phosphate dihydrate, and the like.

Applicants' U.S. Patent No. 4,122,163 describes dentifrices formulated with highly purified calcined kaolin particles from which titanium impurities have been excluded. The patent also describes replacement of the kaolin with other dental abrasive materials including talc, but it does not recognize that the rheological properties of calcined kaolin may be improved thereby or the kaolin need not be specially purified in order to be successfully employed, nor does it disclose that the overall performance of the abrasive can in fact be improved.

The prior art calcined kaolin dentifrices have all encountered formulation problems due to the dilatancy of the material when provided in paste form. In addition, they encounter shelf life problems when used with certain anticariogenic additives.

Thus, prior art materials intended for use as cleaning and polishing constituents of dentifrice preparations have not been entirely satisfactory in one or more of the following respects: relatively poor

cleaning and polishing performances (especially with respect to prevention of reaccumulation of dental calculus, pellicle, materia alba, and the more resistant forms of oral hard tissue stains and pigmentations); incompatibility with fluoride and stannous ion-containing anticariogenic agents; adverse abrasion; difficult, expensive manufacturing requirements; and rinsing and rheological problems.

5 The applicants' US-A-4108979 discloses dentifrice preparations which include a compatible dental abrasive selected from a list which includes, inter alia, calcined kaolin and talc, or a mixture of two or more abrasives. The talc is treated as equivalent to the calcined kaolin, and there is no suggestion to formulate specifically a mixture of calcined kaolin and talc.

10 In accordance with one aspect of the present invention, there is provided a method of improving the rheological properties of a dentifrice preparation comprising calcined kaolin as a cleaning and polishing agent, the method comprising the step of incorporating into the cleaning and polishing agent from 10 to 78% talc by weight of the cleaning and polishing agent.

According to another aspect of the present invention, there is provided a dentifrice preparation having enhanced enamel polishing ability, reduced dentin abrasion, improved whiteness, and improved
15 rheological properties, the dentifrice preparation comprising as a cleaning and polishing agent a mixture comprising from 20 to 88% calcined kaolin, from 10 to 78% talc, and from 2 to 20% of titanium dioxide, all by weight of the mixture.

Preferably the particles are predominantly (i.e. at least 50% by weight) less than about 10 μm (microns) in diameter, and the mixture when formulated into a dentifrice has a whiteness score of at least about 79%.

20 It has been further found that the novel cleaning and polishing agents of the present invention may be used with non-toxic amounts of water-soluble anticariogenic adjuvants such as sodium fluoride or stannous fluoride. It is especially preferred to employ a 1:2 molar mixture of sodium fluoride and stannous fluoride.

Preferably the cleaning and polishing agent is present as from 20 to 95%, by weight of the dentifrice
25 preparations.

It has likewise been discovered that the regular applications of the dentifrice preparations of the present invention to the teeth provides a novel method for cleaning and polishing teeth and for reducing the incidence of gingival disease.

Through the use of the cleaning and polishing agents of the present invention the difficulties
30 experienced with prior art dentifrice cleaning and polishing agents may be overcome, and compositions of the present invention may therefore be used to formulate dentifrices with superior cleaning and polishing capabilities, with enhanced anticariogenic agent compatibilities, greater fluoride uptake by the dental enamel, and with improved rheological properties.

Accordingly, the present invention can provide a cleaning and polishing agent which is capable of
35 reducing the reformation of dental calculus and the incidence of gingivitis and yet which is suitable for incorporation in a dentifrice preparation.

Another object of the present invention is to provide an anticalculus cleaning and polishing agent of the character described which is effective in removing pellicle and dental enamel stains and pigmentations.

Another object of the present invention is to provide anticalculus dentifrice preparations incorporating
40 a cleaning and polishing agent of the character described.

A still further object is to provide a dentifrice preparation incorporating at least one fluoride-containing anticariogenic adjuvant in combination with an anticalculus cleaning and polishing agent of the character described which further serves to enhance the effectiveness of the anticariogenic adjuvant.

45 Description of the drawing

Figures 1—4 are graphs plotting shear force versus shear rate for four series of paired experimental dentifrices demonstrating the improvement of calcined kaolin dentifrices containing talc formulation modifiers.

50 Description of the preferred embodiments

In accordance with the subject invention, it has been discovered that the rheological properties such as shear thinning and dilatancy of calcined kaolin dentifrices are improved substantially by incorporating talc therewith. Shear thinning is especially important in that it improves the efficiency of tube filling during packaging and the extrudability and dispersibility during use by the consumer. Improvement in rinsability
55 has also been noted.

It has also been found that optimal cleaning and polishing characteristics for a dentifrice cleaning and polishing agent are exhibited by a mixture of calcined kaolin, talc as an abrasive and formulation modifier, and titanium dioxide as a whitener and polishing enhancer. The mixture particles are at least predominantly (i.e., 50% or more by weight) less than about 10 microns in diameter, and the mixture when
60 formulated into a dentifrice has a whiteness score of at least 79%. Whiteness as used herein is determined in accordance with the procedure described hereinafter in detail using a wave-length of 450 nanometers.

In addition, it has been found that the cleaning and polishing agent mixture may be advantageously used with water-soluble fluoride-ion-containing anticariogenic adjuvants such as sodium fluoride, NaF, stannous fluoride, SnF_2 , or, preferably, a 1:2 molar mixture thereof.

65 As a result of the foregoing, the cleaning and polishing compositions of the present invention find

utility in therapeutic dentifrices (i.e., dentifrices containing at least one anticariogenic ionic adjuvant in combination with a compatible cleaning and polishing agent and designed to reduce the incidence and severity of dental caries) or dentifrices which, although not containing fluorides or other anticariogenic agents, nonetheless have therapeutic utility in reducing gingival disease.

Cleaning and polishing agents

The calcined kaolin employed in accordance with this invention may be obtained by calcining (i.e., heat treating) kaolinite, $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_2]$, which has been mined, cleaned, dried and fractionated. Prior to calcining, the material may, but need not, be subjected to purification procedures involving magnetic separations or the flocculation and related steps described in U.S. Patent No. 3,477,809 in order to remove impurities.

The purified material is calcined at a temperature lying in the range of about 950°C. to 1150°C. If the temperature does not reach 950°C., the purified kaolinite remains predominantly meta-kaolin, a material which is insufficiently hard to clean and polish satisfactorily from a dental standpoint. Material which has been calcined at about 950°C. is predominantly gamma alumina generally taking the form of spinel-type crystals. However, if the purified material is more highly calcined, (i.e., is subjected to temperatures of up to about 1150°C.), the gamma alumina undergoes a change to highly crystalline mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), generally taking the form of small, needle-like crystals. If the materials are overcalcined (i.e., subjected to temperatures of about 1250°C. or more), larger mullite crystals and materials such as cristobolite (SiO_2) are formed. Material containing large amounts of cristobolite and large mullite crystals are unsatisfactory from a dental standpoint because of their tendency to scratch the tooth enamel unless reduced in size by milling or grinding. As a consequence, the purified, calcined kaolins used in accordance with this invention are desirably predominantly of the gamma alumina and/or mullite form.

After calcining, in which the material agglomerates into large masses, grinding and/or milling must be used to obtain an abrasive having a particle size distribution lying in the range found to be useful in dentifrice preparations.

When lower calcining temperatures are employed (i.e., in the range of about 950°C. to 1050°C.), more economical dry grinding processes such as conventional Bauer-milling, may be employed. However, where higher calcining temperatures of 1050°C. and especially about 1150°C. are employed, it has been found that the relatively greater amounts of hard crystalline material formed at these temperatures may most conveniently be treated by using known wet-sand grinding procedures. Sand grinding techniques may be employed with all of the abrasives of this invention although, as noted, for reasons of economy, it is preferred to use Bauer-milling treatments for materials calcined in the lower temperature ranges. Bauer-milling procedures may be employed with materials calcined in the range of about 1150°C., but it is preferred to use sand grinding techniques with these materials.

Properties of several typical calcined kaolins that may be used in accordance with this invention are given in Table I.

EP 0 102 695 B1

TABLE I
Calcined kaolin properties

	Physical properties	Sample I	Sample II	Sample III
5	Median Particle Size (micrometers)	1.8	0.7	1.4
	Particle Size (% <2 micrometers)	56	82	68
10	Fineness (% retain on 325 mesh)	0.01	0.01	0.02
	Brightness (%)	94	91	91
	Oil Absorption (%)	55	90	53
15	pH (20% solids)	5.5	6.0	5.5
	Specific Gravity	2.63	2.65	2.65
20	Refractive Index	1.62	1.56	1.56
	Bulking Values (ml/g) [gallons/pound]	0.383 [0.046]	0.376 [0.045]	0.376 [0.045]
25	Moisture (% maximum)	0.5	0.5	0.5
	Chemical Analysis (%)			
	Aluminum Oxide	—	44.48	44.48
30	Silicon Dioxide	—	52.41	52.41
	Titanium Dioxide	—	1.79	1.79
	Ferric Oxide	—	0.58	0.58
35	Calcium Oxide	—	0.03	0.03
	Magnesium Oxide	—	0.02	0.02
40	Sodium Oxide	—	0.28	0.28
	Potassium Oxide	—	0.15	0.15
	Ignition Loss	—	0.20	0.20

Especially suitable calcined kaolins include Kaopolite 1147, available from Kaopolite, Inc., and WHITETEX and AL-SIL-ATE S, available from Freeport Kaolin Company. Where desired, mixtures of two or more calcined kaolins in accordance with this invention may be employed.

The talc modifier may be substantially any high quality talc containing low levels of calcium and other elements incompatible with anticarcinogenic adjuvants. One especially suitable talc is 141 Talc U.S.P., a bacterial controlled talc available from Whittaker, Clark & Daniels, Inc. Another suitable talc is Cercron talc No. MP96-28 available from Pfizer, Inc. Typical properties of useful talcs are given in Table II.

EP 0 102 695 B1

TABLE II
Talc properties

	Physical properties	Sampl I	Sample II	Sample III
5	Median Particle Size (micrometers)	5	12	8
	Particle Size (% <2 micrometers)	24	2	17
10	Fineness (% retain on 325 mesh)	0	17	1
	Brightness (%)	89	91	88
	pH (20% solids)	8.7	8.8	9.0
15	Specific gravity	2.70	2.70	2.80
	Tapped Bulk Density (g/cm ³) [pounds/cubic foot]	0.64 [40]	0.94 [59]	0.86 [54]
20	Moisture (% maximum)	0.5	0.5	0.2
	Chemical Analysis			
	Magnesium Oxide	32	30	32
25	Silicon Dioxide	62	61	62
	Calcium Oxide	0.2	0.09	0.5
30	Aluminum Oxide	0.6	0.9	0.5
	Ferric Oxide	1.0	0.9	1.0
	Titanium Dioxide	—	0.05	—
35	Sodium Oxide	—	0.07	—
	Potassium Oxide	—	0.01	—
40	Ignition Loss	5.0	5.13	5.0

Whiteness of the abrasive mixture is enhanced by adding a minor amount (i.e., about 2—20%, by weight of the mixture) of titanium dioxide as a whitening agent. Preferably, about 5—15% titanium dioxide, by weight, is present.

45 The cleaning and polishing mixture of this invention comprises at least about 20% calcined kaolin, at least about 10% talc, and, preferably, about 2—20% titanium dioxide, all by weight of the total cleaning and polishing mixture. It is especially desired that the mixture comprise about 60—80% calcined kaolin, about 5—15% titanium dioxide and balance talc. An especially preferred mixture comprises about 75% calcined kaolin, about 20% talc, and about 5% titanium dioxide.

50 Exemplary abrasive mixtures in accordance with this invention are set forth in the following examples.

Example I

	Abrasive ingredient	Parts by weight
55	Calcined Kaolin I	27.0
	Talc I	7.0

60

65

EP 0 102 695 B1

Example II

	Abrasive ingredient	Parts by weight
5	Calcined Kaolin II	15.0
	Talc II	15.0
10	Titanium Dioxide	2.0

Example III

	Abrasive ingredient	Parts by weight
15	Calcined Kaolin I	22.0
	Calcined Kaolin II	7.0
	Talc I	7.0
20	Titanium Dioxide	1.0

Dentifrice preparations

The mixture of cleaning and polishing agents of the present invention is employed in dentifrice preparations within the range of about 10 up to about 95%, by weight, depending upon the particular formulation desired, as is well known to one skilled in the art.

Toothpastes preferably contain a total of about 20—70% cleaning and polishing mixture, by weight, whereas tooth powders contain about 60—90% cleaning and polishing mixture, by weight. Liquid dentifrices typically employ about 10—40%, by weight, abrasive, whereas gel type dentifrices utilize about 20—40% cleaning and polishing mixture, by weight.

Dentifrice preparations utilizing the cleaning and polishing agents of the subject invention are prepared in a conventional manner and usually include additional ingredients which render the overall composition commercially acceptable to consumers.

Thus, toothpastes require a binder substance to impart desired textural properties. Natural gum binders such as xanthan, tragacanth, gum karaya, gum arabic and guar and seaweed derivatives such as carrageen and alginates, and water-soluble cellulose derivatives, such as methyl cellulose, sodium carboxymethyl cellulose, and hydroxyethyl cellulose, can be used for this purpose. Synthetic colloidal magnesium silicate, such as those available under the trademark "Laponite", also may be used and is preferred in gel-type formulations. Desirably, those materials are employed which are most compatible with fluoride and stannous ions. Improvements in texture can also be attained by including an additional material such as colloidal magnesium aluminum silicate (available under the trademark "VEEGUM") and other smectite clays and fumed silica. Binders in an amount of from 0.5% to 5.0%, by weight, can be used to form a satisfactory toothpaste.

Toothpastes conventionally contain organic surface-active agents, which may be anionic, cationic, nonionic, or ampholytic in nature. Preferably, the agent possess detergent and foaming properties as well. Suitable sudsing agents include, but are not limited to, water-soluble alkyl sulfates having from 8 to 18 carbon atoms in the alkyl radical, such as sodium lauryl sulfate, water-soluble salts of sulfonated monoglycerides of fatty acids having from 10 to 18 carbon atoms in the alkyl radical such as sodium coconut monoglyceride sulfonate, salts of fatty acid amides of taurines such as sodium-N-methyl palmitoyl taurine, and salts of fatty acid esters of isethionic acid.

Other particularly suitable surface-active materials include nonionic agents such as condensates of sorbitan monostearate and ethylene oxide, copolymers of the poly(oxypropylene)-poly(oxyethylene) type (e.g., that known by the registered Trade Mark Pluronic) and amphoteric agents such as quaternized imidazole derivatives (e.g. that known by the registered Trade Mark Miranol). Useful cationic surface-active germicides and antibacterial compounds include tertiary amines containing one fatty alkyl group and two poly(oxyethylene) groups, benzyl dimethyl stearyl ammonium chloride, and diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride. Surface-active agents can be used in the compositions of this invention in an amount of from about 0.5% to about 5.0%, by weight, of the total composition.

Cationic antibacterial agents may be included in compositions of the present invention. Such agents among others include quaternary ammonium compounds, such as benzethonium chloride and cetylpyridinium chloride, and biguanides, such as chlorhexidine, alexidin, hexetidin, and polyhexamethylene biguanide hydrochloride sold under the registered Trademark (Cismocil CQ). These agents may be used in effective amounts ranging from about 0.01 to 5 percent by weight of the dentifrice.

It is also desirable to include some humectant material in a toothpaste to keep it from hardening.

EP 0 102 695 B1

Materials commonly used for this purpose include glycerin, sorbitol, and other polyhydric alcohols. The humectants can comprise up to 35% of conventional toothpaste compositions. In the case of gel-type formulations, humectants may be used at levels as high as 80%, by weight.

Finally, flavoring materials may be included in a toothpaste formulation including small amounts of oils of spearmint, wintergreen and peppermint or other natural or synthetic flavors and sweetening agents such as saccharin, cyclamate, aspartame, dextrose, and levulose.

The non-fluoride dentifrices of this invention generally are employed at their natural pH values which lie in the range of about 6.0—8.0, although, if desired, the pH may be adjusted in the range of about 4.0—9.0 with carboxylic acids, various sodium phosphates or other buffering agents.

Compositions of exemplary dentifrice preparations employing the cleaning and polishing agents of the present invention are given in the following Examples.

Example IV

Ingredient	Parts by weight
Calcined Kaolin I	24.00
Calcined Kaolin II	7.00
Talc I	7.00
Titanium Dioxide	1.00
Glycerin	7.00
Sorbitol (70%)	24.00
Distilled Water	24.92
Magnesium Aluminum Silicate	0.78
Hydroxyethyl Cellulose	0.75
Trisodium Citrate Dihydrate	0.25
Sodium Lauryl Sulfate	1.50
Flavors, Sweeteners and Preservatives,	1.80

Example V

Ingredient	Parts by weight
Calcined Kaolin II	19.00
Talc II	19.00
Titanium Dioxide	2.00
Glycerin	12.00
Sorbitol (70%)	12.00
Distilled Water	31.05
Laponite (registered Trade Mark) D	0.30
Sodium Carboxymethyl Cellulose	1.55
Sodium Citrate Dihydrate	0.25
Sodium Lauryl Sulfate	1.50
Flavors, Sweeteners and Preservatives.	1.35

EP 0 102 695 B1

Example VI

	Ingredient	Parts by weight
5	Calcined Kaolin III	23.00
	Talc III	12.00
	Titanium Dioxide	5.00
10	Glycerin	5.00
	Sorbitol (70%)	23.00
15	Distilled Water	27.15
	Laponite D	0.30
	Sodium Carboxymethyl Cellulose	1.35
20	Sodium Citrate Dihydrate	0.25
	Sodium Lauryl Sulfate	1.50
25	Flavors, Sweeteners and Preservatives	1.45

As previously indicated, the cleaning and polishing agents of the present invention also function as compatible carriers for anticariogenically-effective and non-toxic amounts of water-soluble fluoride-containing anticariogenic adjuvants in anticariogenic dentifrice preparations. Preferably, the adjuvant is present in the form of water-soluble fluoride-containing compounds capable of supplying fluoride. The preferred adjuvant is a 1:2 molar mixture of sodium fluoride, NaF, and stannous fluoride, SnF₂, although other materials such as sodium monofluorophosphate, stannous fluorozirconate (SnZrF₆), indium fluorozirconate (InZrF₇) and complex zirconium-germanium fluorides (e.g. Zr(GeF₆)₂, ZrGeF₈, Ge(ZrF₆)₂, and ZrOGeF₆) may be employed. Sodium fluoride and stannous fluoride are preferred by reason of anticariogenic effectiveness obtainable therewith.

Other suitable adjuvants include water-soluble fluoride salts such as SnF₄, KF, InF₃, PbF₂, FeF₂, NH₄F, and LiF, as well as more complex water-soluble fluoride-containing adjuvants such as fluorosilicates, e.g., Na₂SiF₆, other fluorozirconates, e.g. CaZrF₆, Na₂ZrF₆, K₂ZrF₆, fluorostannites, e.g. NaSnF₃, fluoroborates, e.g. NaBF₄, fluorotitanates, e.g. NaTiF₅, other fluorogermanates, e.g. K₂GeF₆, and mixed halides, e.g., SnClF and Sn₂ClF₃. Mixtures of suitable adjuvants may also be utilized. Another suitable adjuvant comprises a mixture of a fluoride salt and an active phosphate compound such as Victamide as set forth and described in U.S. Pat. No. 3,666,855.

In general, an anticariogenic dentifrice preparation produced in accordance with the subject invention will contain from about 0.05 up to 1.0%, by weight of the dentifrice preparation, of the fluoride-containing anticariogenic adjuvant so as to desirably provide about 1000 ppm fluoride ion. Sodium fluoride is preferably provided at a level of 0.22%, by weight, and when SnF₂ is utilized, the desired amount is preferably about 0.4%. As noted, it is especially desired to employ a 1:2 molar ratio of sodium fluoride and stannous fluoride.

Preferably, such fluoride-containing dentifrice preparations are employed in their natural pH ranges (i.e., about pH 3 to pH 8, although, if desired, the pH range may be adjusted to about pH 4 to pH 9 with various buffering agents.

Exemplary formulations of fluoride-containing dentifrices in accordance with this invention are given in the following examples.

EP 0 102 695 B1**Example VII**

	Constituent	Parts by weight
5	Calcined Kaolin I	22.00
	Calcined Kaolin II	7.00
	Talc I	7.00
10	Titanium Dioxide	2.00
	Glycerin	7.00
15	Sorbitol (70%)	24.0
	Distilled Water	24.0
	Magnesium Aluminum Silicate	0.78
20	Hydroxyethyl Cellulose	0.75
	Sodium Lauryl Sulfate	1.50
25	Citric Acid	0.96
	Sodium Hydroxide	0.25
	Sodium Fluoride	0.05
30	Stannous Fluoride	0.33
	Flavors, Sweeteners and Preservatives	2.38

Example VIII

	Ingredient	Parts by weight
	Calcined Kaolin (U.S. Patent 4,122,163)	18.00
40	Talc III	18.00
	Titanium Dioxide	4.00
45	Glycerin	5.00
	Sorbitol (70%)	23.00
	Distilled Water	27.03
50	Laponite D	0.30
	Sodium Carboxymethyl Cellulose	1.35
55	Sodium Citrate Dihydrate	0.25
	Sodium Lauryl Sulfate	1.50
	Sodium Fluoride	0.22
60	Flavors, Sweeteners and Preservatives.	1.35

65

EP 0 102 695 B1

Example IX

	Ingredient	Parts by weight
5	Calcined Kaolin II	19.00
	Talc II	19.00
	Titanium Dioxide	2.00
10	Glycerin	12.00
	Sorbitol (70%)	12.00
15	Distilled Water	29.25
	Xanthan Gum	1.55
	Sodium Citrate Dihydrate	0.25
20	Sodium Lauryl Sulfate	1.50
	Potassium Acid Phthalate	1.00
25	Stannous Fluoride	0.41
	Flavors, Sweeteners and Preservatives.	2.04

Experimental evaluations

30 The superiority of the purified, calcined kaolin cleaning and polishing compositions disclosed herein has been substantiated by the following experimental evaluations.

1. Enamel polish procedure.

35 Enamel polish was determined with specially prepared teeth that were chemically dulled and then polished with a slurry of an abrasive or dentifrice using an automatic toothbrushing machine. The degree of polish was determined with a reflectometer that measured the intensity of specular light reflected by the treated tooth specimens. The greater the intensity of the reflected light from a specimen, the higher was the luster of the tooth and consequently the higher was the numerical polish score. The details of this procedure have been previously described in detail in Putt et al., *J. Dent. Res.* 59:1177 (1980).

40 2. Cleaning procedure.

The degree of cleaning was assembled by measuring the amount of plastic removed by brushing with abrasive slurries. The amount of plastic removed was quantitated by profilometry. The greater the quantity of plastic removed by the brushing treatment, the deeper was the abraded area, and consequently, the higher was the cleaning score.

45 All evaluations were made on Plexiglas blocks that were cut and milled from 0.64 cm (1/4 inch) thick sheets into 2-cm squares. Brushing treatments were administered with the V-8 Crossbrushing Machine at a pressure of 300 grams for 2000 strokes. Abrasive slurries were prepared by mixing one part of abrasive by weight with 2 parts of a 1% sodium carboxymethyl cellulose solution.

50 Surface profile measurements were made with a profilometer. This instrument is a surface topography measurement and analysis system utilizing a diamond stylus with a tip radius of 0.003 mm (0.0001 inch). The stylus traces the surface of a specimen and produces an analog signal that is an exact replica of the traced surface topography. The signal that is produced can be recorded on a strip chart in its original form or modified and analyzed prior to recording. In the analysis of Plexiglas specimens, the high-frequency roughness signals were electronically filtered from the original signal. Cleaning scores were reported in micro-inches as mean depth measurements of the abraded area. The mean depth was determined by dividing the area of the abraded cross section of each profilometer trace by the width of the abraded area. The area of the cross section was measured with a planimeter, providing a quantitative representation of the extent of material loss along the path traced. This value is used as an absolute measure of the ability of the abrasive slurry to remove plastic from the block.

60 The foregoing laboratory assessment of cleaning correlates well with cleaning observations in human clinical investigations as well as the RDA method of measuring dentin abrasion described below.

3. Dentin abrasion procedure.

65 The dentin abrasion procedure measures the relative abrasiveness of a dentifrice compared to a

standard material. Quantitative determination of abrasivity was accomplished by brushing radioactive dentin with a suspension of a dentifrice. The amount of dentin abraded was proportional to the abrasiveness of the dentifrice tested and was measured by the level of radioactivity in the suspension after the brushing treatment. The procedure has been described previously in Hefferren, *J. Dent. Res.* 55:563, 1976.

4. Instrumental method of measuring whiteness.

Whiteness of dentifrice samples was determined by a procedure similar to TAPPI test method T-646 using a DU Spectrophotometer (Model 2400) with a Diffuse Reflectance Attachment (Model 2580). The diffuse reflectance attachment measures the diffuse reflectance of opaque liquid or solid samples relative to a standard. Radiation from a tungsten lamp is dispersed by a prism and the wavelength is manually set. The monochromatic light strikes the sample surface and diffuse light reflected upward from the sample at angles between 35° and 55° strikes an ellipsoidal mirror, passes through an opal glass diffusing screen to the photodetector.

The reflectance observed at 450 nm is representative of the visual whiteness of the sample using magnesium oxide as the reflectance standard.

5. Dentifrice rheology

The rheology of dentifrice samples was determined by means of a Brookfield Viscometer (Model RVT) equipped with a T-Bar F spindle and a Helipath stand. Dentifrice samples were extruded into a 150 ml beaker and allowed to stand for 24 hours. Viscometer readings were made at eight different rotational speeds at the midpoint of descent and ascent 1.5 cm below the paste surface.

Using the foregoing technique dentifrices and abrasives in accordance with this invention were evaluated as follows. Enamel polish data were obtained using the foregoing technique for water slurries of a series of mixtures of talcs (Table II above) with different kaolins, namely, calcined kaolins I, II and III (Table I above) and the purified calcined kaolin of U.S. Patent No. 4,122,163. These enamel polish data are provided in Table III. The data show that superior polishing results are achieved with water slurries of all calcined kaolin-talc mixtures containing about 20% or more calcined kaolin. The data also show that talc in fact enhances the polishing ability of many of the mixtures relative to either constituent alone.

TABLE III
Enamel polish of water slurries of calcined kaolins and talc

	Ratio of calcined kaolin to talc I	Polish score*			
		Calcined kaolin I	Calcined kaolin II	Calcined kaolin III	Purified calcined kaolin**
1:0		104±1	96±1	100±2	103±2
4:1		110±1	99±1	106±1	111±1
3:2		112±1	104±2	107±1	112±1
2:3		112±1	107±1	110±1	112±2
1:4		91±4	94±2	108±1	108±2
0:1		40±2	40±1	49±2	40±2

* Means ± standard error of 6 replicates.

** U.S. Patent 4,122,163.

Table IV reports cleaning scores for various mixtures of calcined kaolin and talc. These data also demonstrate that such mixtures containing at least about 20% calcined kaolin perform extremely well from a cleaning standpoint.

EP 0 102 695 B1

TABLE IV
Cleaning of mixtures of calcined kaolin and talc

	Ratio calcined kaolin III to talc I	Cleaning scores (μ in)*
5	1:0	190 \pm 11
10	4:1	173 \pm 6
	3:2	151 \pm 9
	2:3	110 \pm 11
15	1:4	88 \pm 6
	0:1	24 \pm 4

* Mean \pm standard error of 8 replicates.

Cleaning and dentin abrasion scores were obtained using the foregoing procedures for a number of dentifrices incorporating calcined kaolin abrasives, some containing talc. For comparative purposes, scores were also obtained for dentifrices containing other abrasive systems. The data are presented in Table V. In all cases, cleaning performance was not adversely affected by the presence of talc in the calcined kaolin formulations.

In spite of the success of the calcined kaolin-talc mixtures as cleaning and polishing agents, they are not unduly abrasive. The abrasion data of Table V demonstrate the relative safety and low abrasion for the mixtures of this invention. These data indicate that the addition of talc to calcined Kaolin dentifrices decreases abrasivity to dentin without causing appreciable diminution in cleaning ability.

TABLE V
Cleaning and abrasion of calcined kaolin-talc dentifrices

	Dentifrice abrasive system	Cleaning score* (μ in)	Abrasion score*
35			
40	36% Calcined Kaolin I	112 \pm 4	98 \pm 1
	28% Calcined Kaolin I, 6% Calcined Kaolin III	131 \pm 6	131 \pm 2
	21% Calcined Kaolin I, 6% Calcined Kaolin III, 6% Talc I	120 \pm 6	70 \pm 3
45	21% Calcined Kaolin I, 13% Calcined Kaolin III	147 \pm 8	117 \pm 3
	14% Calcined Kaolin I, 13% Calcined Kaolin III, 6% Talc I	133 \pm 4	98 \pm 3
50	19% Calcined Kaolin III, 19% Talc II	131 \pm 5	94 \pm 5
	37% Purified, Calcined Kaolin (U.S. Patent 4,122,163)	110 \pm 3	97 \pm 4
	CaHPO ₄ · 2H ₂ O, CaCO ₃	66 \pm 4	61 \pm 2
55	CaCO ₃ , Al(OH) ₃	96 \pm 7	101 \pm 4

* Mean \pm standard error of 8 replicates.

Using the described technique for determining whiteness, the whiteness of a series of dentifrice formulations was measured. The tested dentifrices included calcined kaolin alone, mixtures thereof with talc, and the invention combination of calcined kaolin, talc and titanium dioxide. For comparative purposes, the whiteness of dentifrices based of the highly purified calcined kaolin of U.S. Patent No. 4,122,163 was also determined. These data, which are reported in Table VI, demonstrate that the degree of whiteness of calcined kaolin-talc dentifrices in combination with titanium dioxide whiteners is equivalent to that of

EP 0 102 695 B1

calcined kaolin-dentifrices without talc even though talc has a negative effect on the whiteness of calcined kaolins. Off-color calcined kaolins, such as Calcined Kaolins II and III, may be employed in a dentifrice of acceptable whiteness in accordance with this invention.

5

TABLE VI
Whiteness of calcined kaolin dentifrice

	Dentifrice abrasive system	Whiteness (%)
10	40% Calcined Kaolin II	72
	38% Calcined Kaolin II, 2% TiO ₂	79
	20% Calcined Kaolin II, 20% Talc I	68
15	19% Calcined Kaolin II, 19% Talc I, 2% TiO ₂	79
	40% Calcined Kaolin III	69
20	38% Calcined Kaolin III, 2% TiO ₂	79
	19% Calcined Kaolin III, 19% Talc II, 2% TiO ₂	79
	40% Purified Calcined Kaolin (U.S. Patent 4,122,163)	80
25	38% Purified Calcined Kaolin, 2% TiO ₂	82
	19% Purified Calcined Kaolin, 19% Talc II, 2% TiO ₂	82

30

By means of the described technique the rheology of four dentifrice pairs was compared. Each pair of dentifrices included a formulation containing only calcined kaolin as the polishing agent and an identical formulation where a portion of the calcined kaolin was replaced by talc. The data were plotted graphically as shear force (which is proportional to the scale reading) versus shear rate (which is proportional to the speed of rotation) in Figures 1—4 of the drawing.

35

Figures 1—4 demonstrate that the addition of talc to dentifrices containing calcined kaolin reduces viscosity slightly and substantially increases shear thinning, a collective term for the combined effects of thixotropy and pseudoplasticity. This reduction in viscosity which occurs at high shear rates with the talc-containing dentifrices results in improved tube filling, extrusion from the tube, and dispersibility during toothbrushing.

40

In accordance with this invention, it has been discovered that the rheological properties of calcined kaolin-based dentifrices may be remarkably improved by incorporating talc therewith. Further, by employing an additional titanium dioxide additive, the whiteness of off-color calcined kaolin samples may be brought up to acceptable levels.

45

Claims

1. A method of improving the rheological properties of a dentifrice preparation comprising calcined kaolin as a cleaning and polishing agent, the method comprising the step of incorporating into the cleaning and polishing agent from 10 to 78% talc by weight of the cleaning and polishing agent.

50

2. A method as claimed in claim 1, wherein the dentifrice preparation further comprises at least one water-soluble fluoride-containing anticariogenic adjuvant.

55

3. A method as claimed in claim 2, wherein the adjuvant is a mixture of sodium fluoride and stannous fluoride in a molar ratio of about 1:2.

4. A method as claimed in claim 1, 2 or 3, wherein at least 50% by weight of the particles of the cleaning and polishing agent are less than 10 μ m (microns) in diameter.

60

5. A dentifrice preparation having enhanced enamel polishing ability, reduced dentin abrasion, improved whiteness, and improved rheological properties, the dentifrice preparation comprising as a cleaning and polishing agent a mixture comprising from 20 to 88% calcined kaolin, from 10 to 78% talc, and from 2 to 20% of titanium dioxide, all by weight of the mixture.

6. A dentifrice preparation as claimed in claim 5, and further comprising at least one water-soluble fluoride-containing anticariogenic adjuvant.

65

7. A dentifrice preparation as claimed in claim 6, wherein the adjuvant is a mixture of sodium fluoride and stannous fluoride in a molar ratio of approximately 1:2.

8. A dentifrice preparation as claimed in claim 6 or 7, wherein the anticariogenic adjuvant is present at a level of 0.05—1.0% by weight of the preparation.

9. A dentifrice preparation as claimed in any one of claims 5 to 8, wherein the cleaning and polishing agent is present at a level of from 20 to 95%, by weight of the dentifrice preparation.

5 10. A dentifrice preparation as claimed in any one of claims 5 to 9, and further comprising an effective amount of an antibacterial agent.

11. A dentifrice preparation as claimed in any one of claims 5 to 10, wherein at least 50% by weight of the particles of the cleaning and polishing mixture are less than 10 microns in diameter.

12. A dentifrice preparation as claimed in any one of claims 5 to 11, wherein the mixture comprises
10 from 60 to 80% calcined kaolin, from 5 to 15% titanium dioxide, and the balance talc, all by weight of the mixture.

13. A dentifrice preparation as claimed in any one of claims 5 to 12, wherein the calcined kaolin particles are predominantly of the gamma alumina or mullite form and wherein the dentifrice preparation has a whiteness score of at least 79%.

15

Patentansprüche

1. Verfahren zur Verbesserung der rheologischen Eigenschaften einer Zahnreinigungs-Zubereitung, umfassend calciniertes Kaolin als Reinigungs- und Polier-Mittel, wobei das Verfahren die Stufe der
20 Einverleibung in das Reinigungs- und Polier-Mittel von 10 bis 78 Gew.-% Talc, bezogen auf das Reinigungs- und Polier-Mittel, umfaßt.

2. Verfahren nach Anspruch 1, wobei die Zahnreinigungs-Zubereitung ferner mindestens einen wasserlöslichen, fluoridhaltigen, antikariogenen Hilfsstoff umfaßt.

3. Verfahren nach Anspruch 2, wobei der Hilfsstoff ein Gemisch von Natriumfluorid und Zinn(II)-fluorid
25 in einem Molverhältnis von etwa 1:2 ist.

4. Verfahren nach Anspruch 1, 2 oder 3, wobei mindestens 50 Gew.-% der Teilchen des Reinigungs- und Polier-Mittels einen Durchmesser unter 10 µm (Mikron) aufweisen.

5. Zahnreinigungs-Zubereitung mit verstärkter Fähigkeit zur Polierung des Zahnschmelzes, verminderter Zahnabnutzung, verbesserter Weißheit und verbesserten rheologischen Eigenschaften,
30 wobei die Zahnreinigungs-Zubereitung als reinigenden und polierenden Wirkstoff ein Gemisch aus 20 bis 88% calciniertem Kaolin, 10 bis 78% Talc und 2 bis 20% Titandioxid, alle bezogen auf das Gewicht des Gemisches, umfaßt.

6. Zahnreinigungs-Zubereitung nach Anspruch 5, umfassend ferner mindestens einen wasserlöslichen fluoridhaltigen, antikariogenen Hilfsstoff.

7. Zahnreinigungs-Zubereitung nach Anspruch 6, wobei der Hilfsstoff ein Gemisch von Natriumfluorid und Zinn(II)-fluorid in einem Molverhältnis von etwa 1:2 ist.

8. Zahnreinigungs-Zubereitung nach Anspruch 6 oder 7, wobei der antikariogene Hilfsstoff in einer Menge von 0,05 bis 1,0 Gew.-% der Zubereitung vorhanden ist.

9. Zahnreinigungs-Zubereitung nach einem der Ansprüche 5 bis 8, wobei der reinigende und
40 polierende Wirkstoff in einer Menge von 20 bis 95 Gew.-% der Zahnreinigungs-Zubereitung vorhanden ist.

10. Zahnreinigungs-Zubereitung nach einem der Ansprüche 5 bis 9, enthaltend ferner eine wirksame Menge eines antibakteriellen Wirkstoffes.

11. Zahnreinigungs-Zubereitung nach einem der Ansprüche 5 bis 10, wobei mindestens 50 Gew.-% der Teilchen des Reinigungs- und Polier-Gemisches einen Durchmesser unter 10 Mikron aufweisen.

12. Zahnreinigungs-Zubereitung nach einem der Ansprüche 5 bis 11, wobei das Gemisch 60 bis 80%
45 calciniertes Kaolin, 5 bis 15% Titandioxid, Rest Talc, alle bezogen auf das Gewicht des Gemisches, umfaßt.

13. Zahnreinigungs-Zubereitung nach einem der Ansprüche 5 bis 12, wobei die Teilchen des calcinierten Kaolins überwiegend aus der Gamma-Aluminiumoxid- oder Mullit-Form bestehen und wobei die Zahnreinigungs-Zubereitung einen Weißheits-Wert von mindestens 79% aufweist.

50

Revendications

1. Un procédé pour améliorer les propriétés rhéologiques d'une préparation dentifrice comprenant du kaolin calciné comme agent à nettoyer et à polir, le procédé comprenant le stade d'incorporation à l'agent à
55 nettoyer et à polir de 10 à 78% de talc relativement au poids de l'agent à nettoyer et à polir.

2. Un procédé selon la revendication 1, dans lequel la préparation dentifrice comprend de plus au moins un adjuvant anticariogène contenant un fluorure soluble dans l'eau.

3. Un procédé selon la revendication 2, dans lequel l'adjuvant est un mélange de fluorure de sodium et de fluorure stanneux dans un rapport molaire d'environ 1/2.

4. Un procédé selon la revendication 1, 2 ou 3, dans lequel au moins 50% en poids des particules de
60 l'agent à nettoyer et à polir ont un diamètre inférieur à 10 µm (micromètres).

5. Une préparation dentifrice ayant un pouvoir accru de polissage de l'émail, une abrasion réduite de la dentine, une meilleure blancheur et des propriétés rhéologiques améliorées, la préparation dentifrice comprenant comme agent à nettoyer et à polir un mélange comprenant de 20 à 88% de kaolin calciné, de
65 10 à 78% de talc et de 2 à 20% de dioxyde de titane, le tout relativement au poids du mélange.

EP 0 102 695 B1

6. Une préparation dentifrice selon la revendication 5, comprenant de plus au moins un adjuvant anticariogène contenant un fluorure soluble dans l'eau.

7. Une préparation dentifrice selon la revendication 6, dans laquelle l'adjuvant est un mélange de fluorure de sodium et de fluorure stanneux dans un rapport molaire d'environ 1/2.

5 8. Une préparation dentifrice selon la revendication 6 ou 7, dans laquelle l'adjuvant anticariogène est présent à un taux de 0,05 à 1,0% du poids de la préparation.

9. Une préparation dentifrice selon l'une quelconque des revendications 5 à 8, dans laquelle l'agent à nettoyer et à polir est présent à un taux de 20 à 95% du poids de la préparation dentifrice.

10. Une préparation dentifrice selon l'une quelconque des revendications 5 à 9, et comprenant de plus
10 une quantité efficace d'un agent antibactérien.

11. Une préparation dentifrice selon l'une quelconque des revendications 5 à 10, dans laquelle au moins 50% du poids des particules du mélange à nettoyer et à polir ont un diamètre inférieur à 10 micromètres.

12. Une préparation dentifrice selon l'une quelconque des revendications 5 à 11, dans laquelle le
15 mélange comprend de 60 à 80% de kaolin calciné, de 5 à 15% de dioxyde de titane, le complément étant du talc, le tout relativement au poids du mélange.

13. Une préparation dentifrice selon l'une quelconque des revendications 5 à 12, dans laquelle les particules de kaolin calciné sont de façon prédominante constituées de la forme γ -alumine ou mullite et la préparation dentifrice a une note de blancheur d'au moins 79%.

20

25

30

35

40

45

50

55

60

65



